Exploring the Structure of Surfactants with 2D Rheo-SANS

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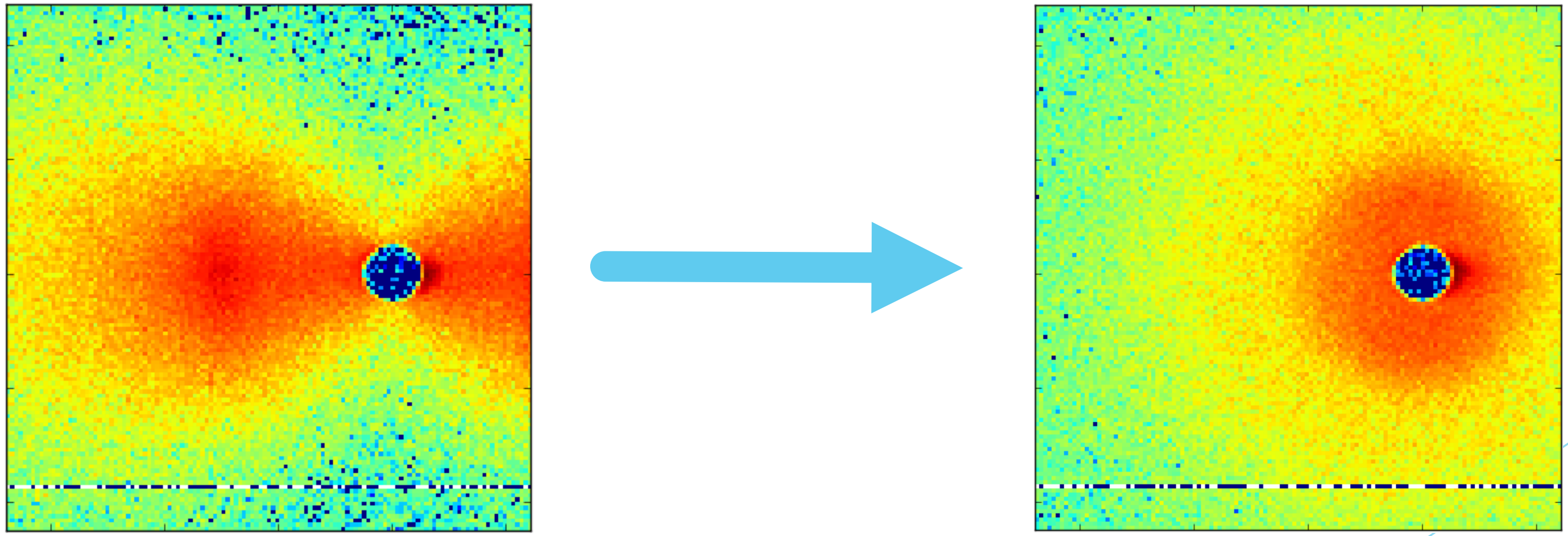
Project Goal

- Understanding the structural evolution of a lamellar surfactant phase at high shear rates using neutron scattering

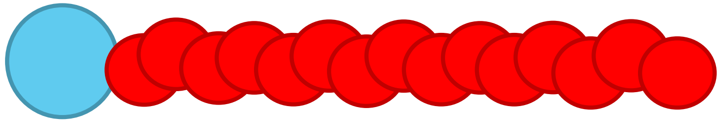


Surfactants

- Surfactants are everywhere:
  - Soaps & Detergents
  - Emulsifiers (like mayonnaise)
  - Drug Delivery
  - Industrial Lubricants

- What are they?
  - Surf(ace) act(ive) ag(ent) =Surf-act-ant

Head Group | Tail

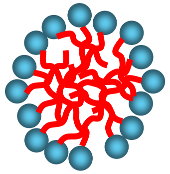


Hydrophilic | Hydrophobic

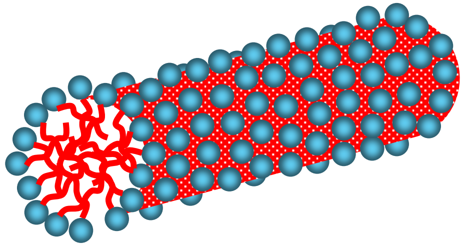
Structures based on geometry of surfactants packing together

Surfactant Packing Parameter(SPP) = $\frac{volume}{area_{head} * length_{tail}}$

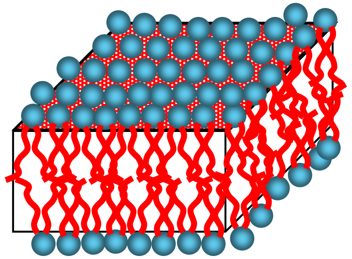
Spherical Micelles



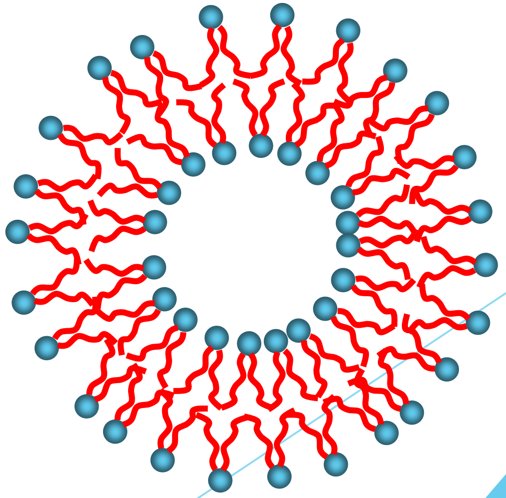
Cylindrical Micelles



Lamellar Sheets



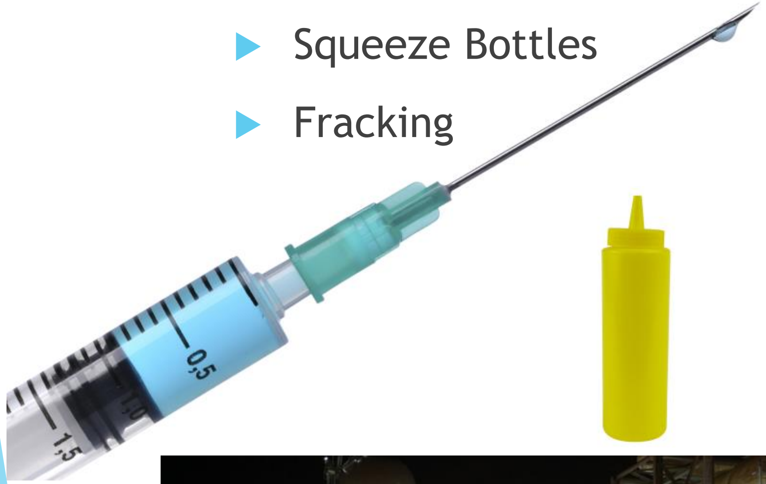
Spherical Bilayer



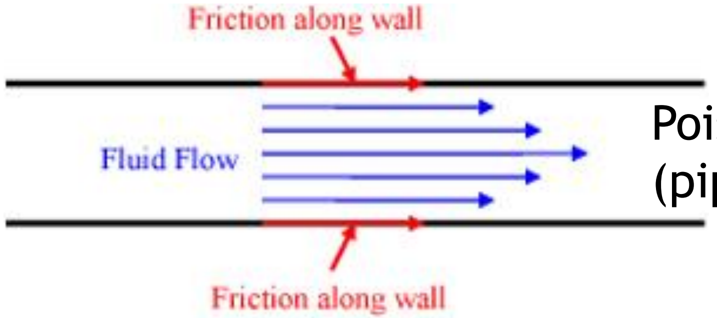
SPP = 1/3 -> 1/2 -> 1

Shear Flow

- Shear flow is everywhere:
  - Needles
  - Pipes
  - Squeeze Bottles
  - Fracking

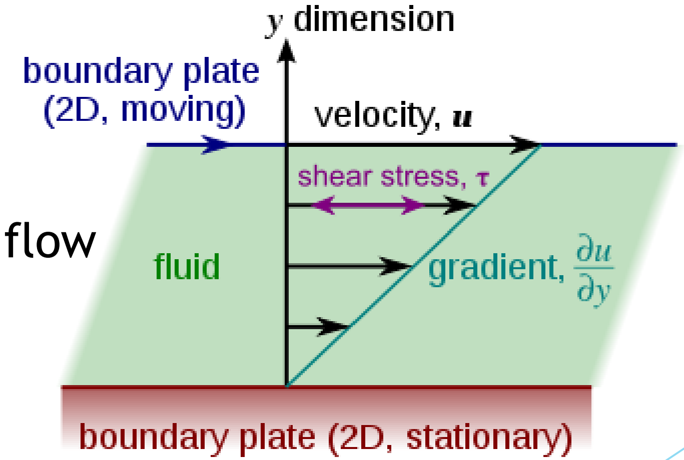


Shear Flow – Gradient of a stress force through a substance

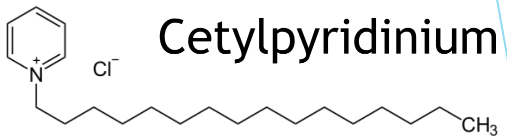


Poiseuille shear flow (pipe flow)

Couette shear flow (sliding cards)



Previous Research- Sponge to Lamellar Phase Collapse



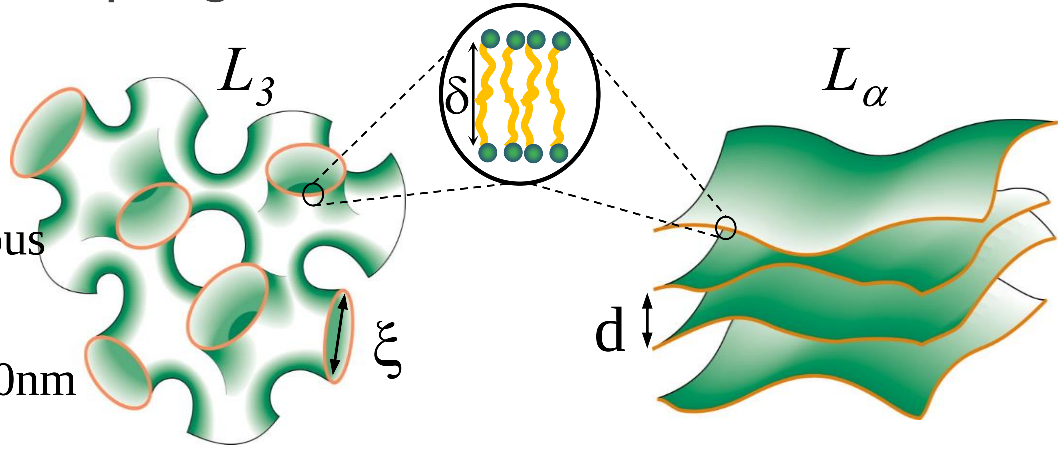
Cetylpyridinium Chloride (CPCl)

Sponge Phase

Lamellar Phase

- Isotropic
- Non viscous

$\xi \sim 1.3d$
~ 10 -100nm



- Ordered
- Viscous

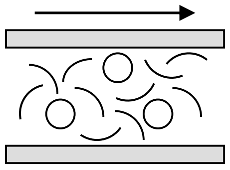
d ~ 2-3nm

While studying phase transitions, a ‘collapse’ was discovered, where at high shear rates the lamellar phase changes abruptly to something unknown

Transition Mechanism

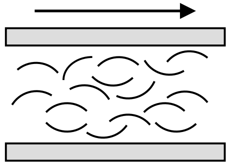
S=sponge, L=lamellar, c=critical

No shear effect



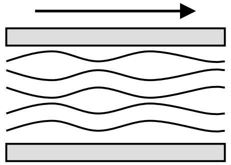
$\dot{\gamma} << \dot{\gamma}_c^S$

Sponge tears apart



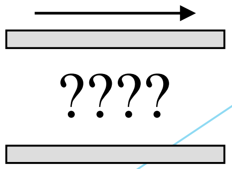
$\dot{\gamma} \sim \dot{\gamma}_c^S$

Lamellar fully-aligned



$\dot{\gamma}_c^S < \dot{\gamma} < \dot{\gamma}_c^L$

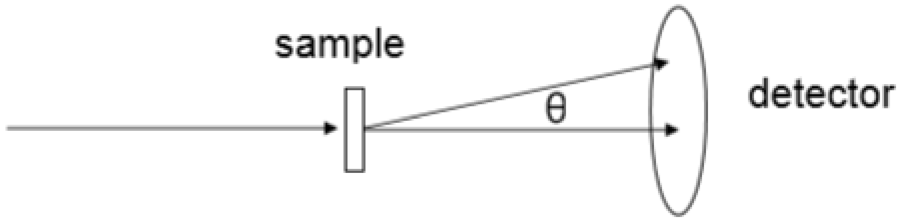
Lamellar “collapses”



$\dot{\gamma} > \dot{\gamma}_c^L$

Small-Angle Neutron Scattering (SANS)

- Neutrons scattered at small angles – $\theta < 2.5^\circ$

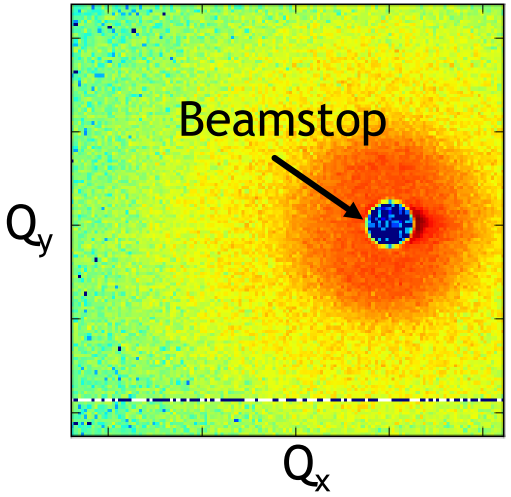


- Q is the scattering vector

$$\boxed{Q = \frac{4\pi}{\lambda}\sin\theta}$$

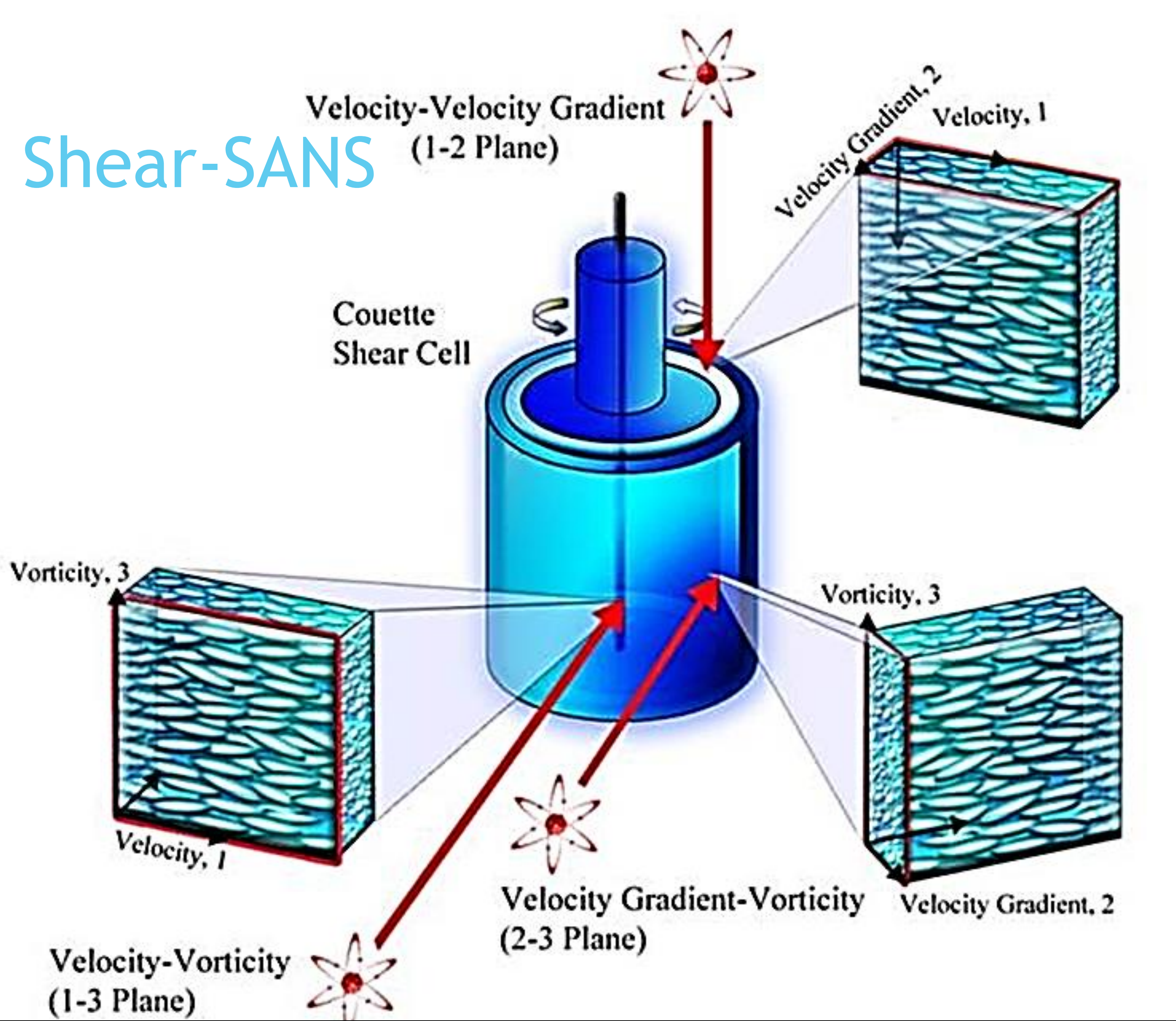
- Bragg peaks occur at highly ordered and ubiquitous distances

$$\boxed{Q = \frac{2\pi}{d}}$$



Large Q = Small Distances
Small Q = Large Distances

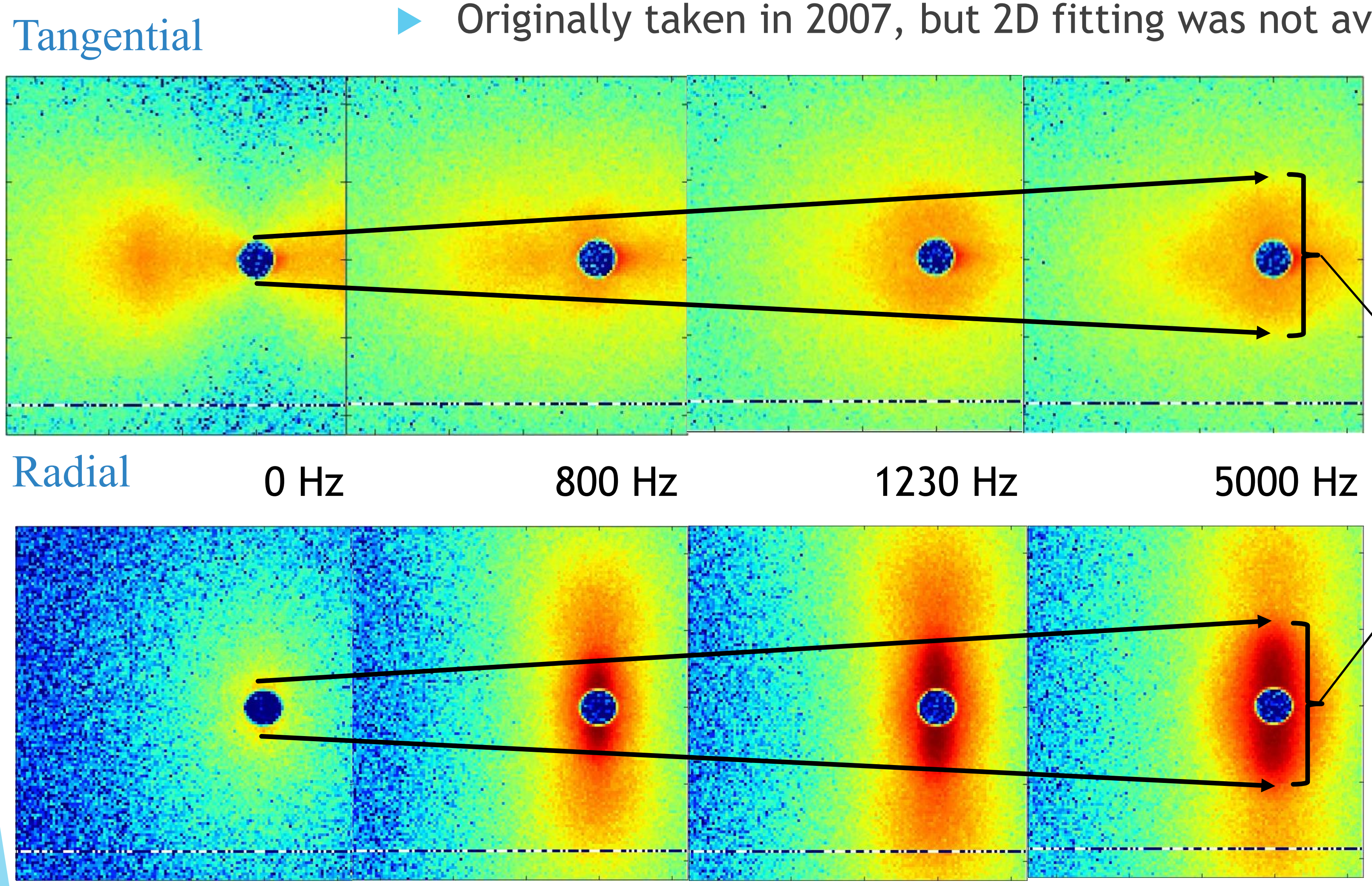
Shear-SANS



In the presence of shear flow, systems which were anisotropic can become oriented

Data

- Typical data fitting uses 1D circular averages
  - For oriented systems, this is a bad approximation
- Originally taken in 2007, but 2D fitting was not available



Note increasing isotropic scattering in tangential with shear rate

Vertical scattering from same part of structure

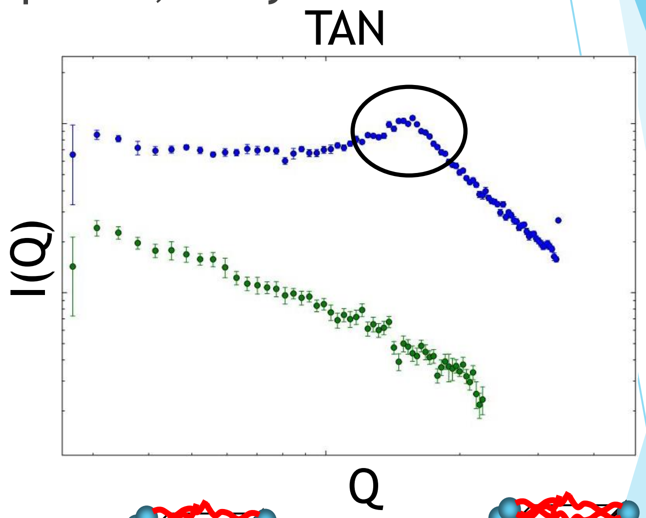
Note increasing anisotropic scattering in radial with shear rate

Hypothesis

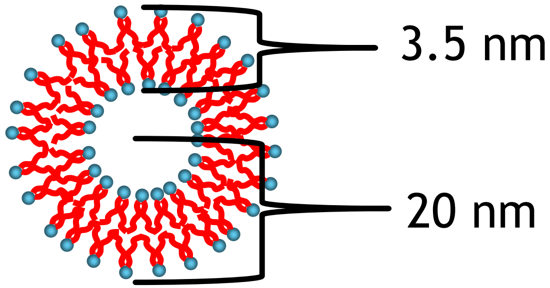
- The lamellar sheets transition to something aligned with the flow, which scatters isotropically in the tangential direction: rods, ellipsoids, or cylinders?

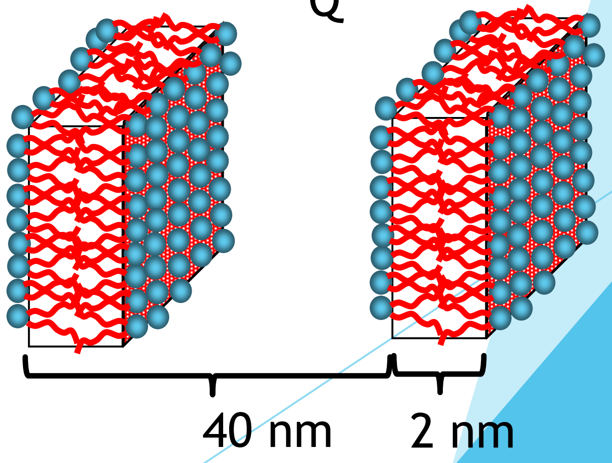
Testing the Hypothesis

- What distances are characteristic?
  - Lamellar
    - Bragg Peak -> lamellar separation - 40 nm
    - Previous work says lamellar thickness is 2.0 nm
  - Aligned structures
    - Maximum surfactant head separation – 3.5 nm
    - Guinier – Radius of Gyration – 20 nm



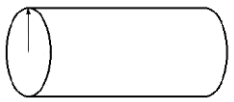
$$I(Q) = I(0)\exp\left(\frac{-R_g^2Q^2}{3}\right)$$



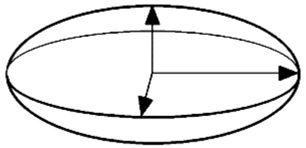


Analysis of Models

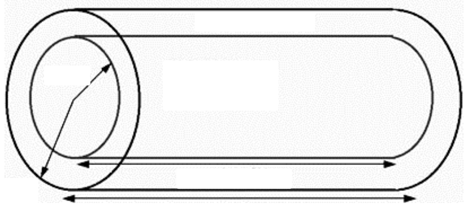
- Rod



  - Could form from lamellar sheets tearing into strips
  - Captures high Q, misses small variations and low Q

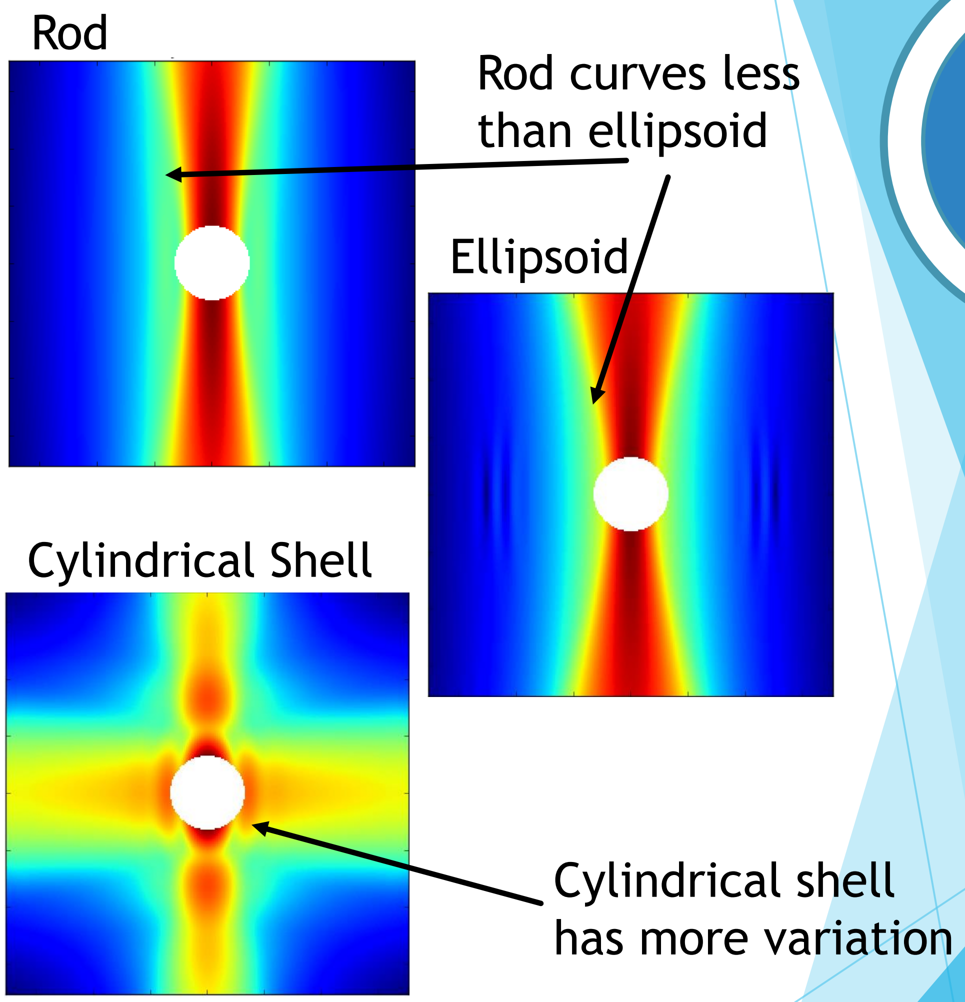


- Ellipsoid
  - Could form from lamellar sheets tearing and balling
  - Can approximate small variations at cost of low Q



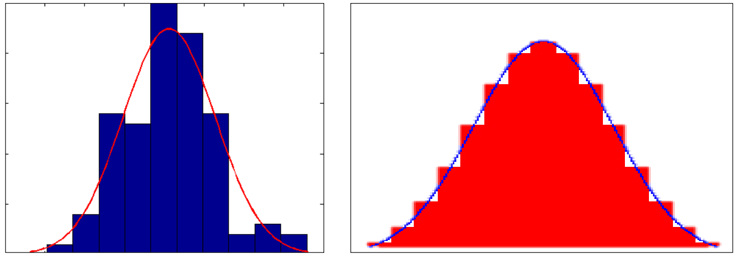
- Cylinder (Shell)
  - Could form from lamellar sheets rolling up and aligning with flow
  - Can match high and low Q, and most small variations

Radial Theoretical Scattering

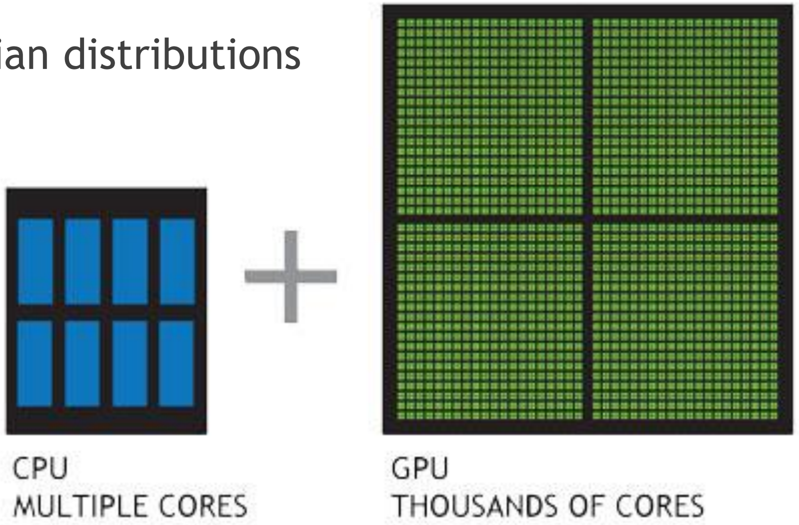


Models calculated with characteristic distances, same for Rod and Ellipsoid, while Cylindrical structure used bilayer constraint

2D Fitting



- Iteration time ~ $q^2(2^n)^m$
  - where q^2 = 128x128 = 16384 pixels
  - n is the number of parameters
  - m is the number of points used to calculate Gaussian distributions

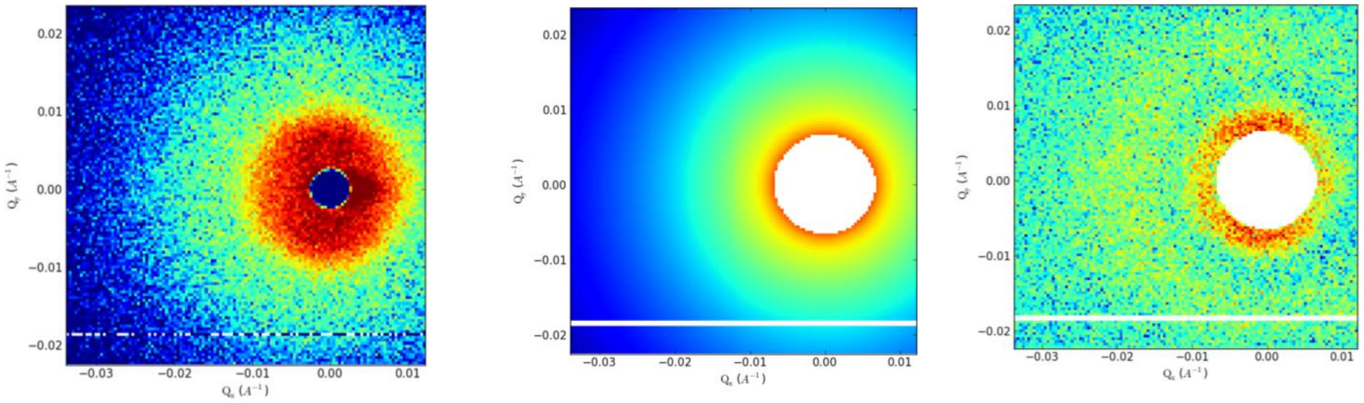


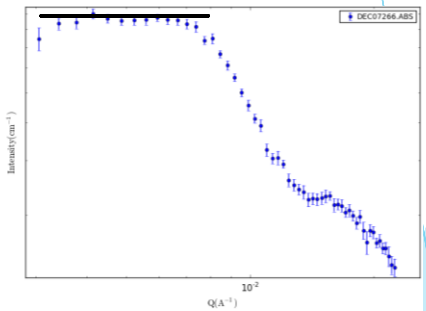
- New Approach: Parallel GPUs!
  - Takes computation intensive code
  - Theoretical reduction in iteration time by x100
- Result: Speed up on single GPU by factor of 15
  - 48 hours of fitting to 3 hours

Fitting Results with Cylindrical Shell

TAN

2350 Hz Data | 2350 Hz Fit | 2350 Hz Residuals

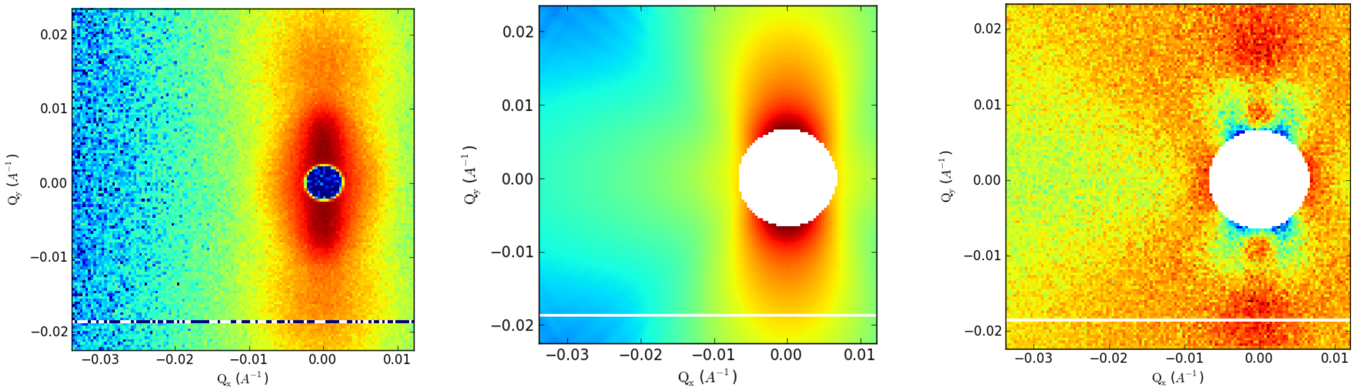




- At low Q scattering shows depression due to structure factor
  - There are currently no orientable structure factors for 2D fits

RAD

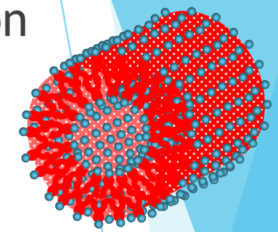
2350 Hz Data | 2350 Hz Fit | 2350 Hz Residuals



Radius = 12 ± 0.1 nm
Length = 250
Shell Thickness = 3 ± 0.1 nm
Chi^2/N = 2.01

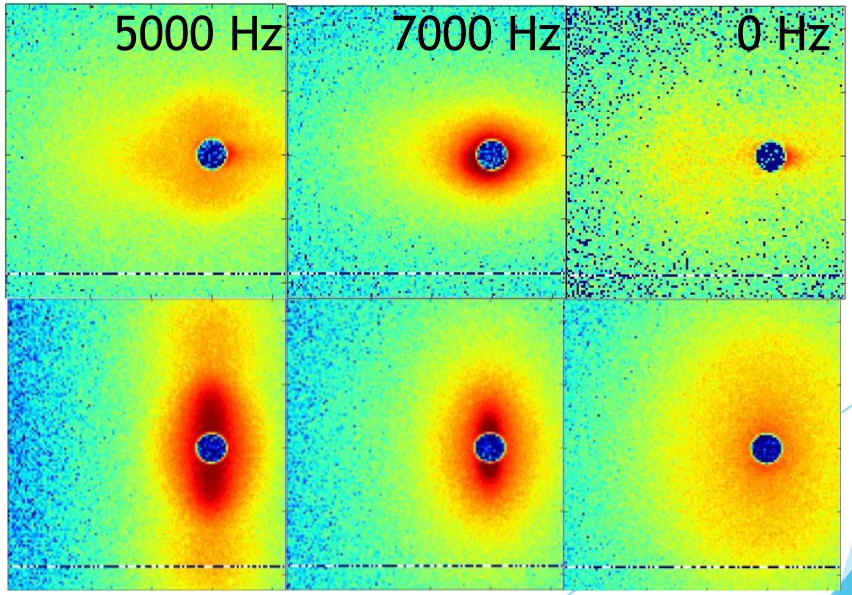
Summary

- 2D fitting requires more computation time but provides orientational information
  - Solution: split computation among faster GPUs to decrease iteration time



- Lamellar phase collapses to long cylindrical bilayer vesicles at shear rates of ~2000 Hz

- Further research:
  - Second ‘collapse’ at 7000 Hz
  - Forms a meta-stable state
  - Extrapolate from first transition



Acknowledgements

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Questions?